HYDROGEN AND CARBON MONOXIDE TEMPERATURE PROGRAMMED DESORPTION STUDY OF Mn-Fe CATALYSTS

Y.Soong, V.U.S. Rao, M.F. Zarochak, and R. J. Gormley
Pittsburgh Energy Technology Center, U.S. Department of Energy,
P.O. Box 10940, Pittsburgh, PA 15236

B. Zhang, Institute of Coal Chemistry, Academia Sinica,
P.O. Box 165, Taiyuan, Shanxi, China

INTRODUCTION

Mn-Fe catalysts have been studied extensively during recent years, primarily because they can enhance the selectivity for low -molecular weight olefins in the Fischer-Tropsch (FT) synthesis (1-9). The reason for the increased selectivity towards light olefins on Mn-Fe catalysts remains controversial. A chemical and/or electronic promoter effect of Mn on the available iron surface has been proposed (4). The change in selectivity upon the addition of Mn to iron catalysts has also been attributed to a MnO species sitting on the Fe surface (1). Moreover, a surface spinel phase ($MnFe_2O_4$) has been proposed to play an important role in providing high selectivity to light olefins (2,3,5,6). It is still an open question as to whether the spinel phase ($MnFe_2O_4$) is responsible for the activity and selectivity during the FT synthesis.

In general, Mn-Fe catalysts were prepared by coprecipitation (or impregnation) of the corresponding nitrates. The degradation of a metal complex, a simple method employed in this study, has not been widely utilized. In this study, $MnFe_2(C_2O_4)_3$ was decomposed to prepare the Mn-Fe catalysts. Some of the major advantages of this method are the following : (a) degradation of this complex can lead to the formation of various Mn-Fe oxides by calcination at different temperatures; and (b) pure Mn-Fe spinel can be prepared with the correct stoichiometric metal ratio, Fe/Mn=2.

Previous studies have reported that hydrogen adsorption on iron catalysts can be activated and dissociative, and carbon monoxide adsorption on iron catalysts includes both associative and dissociative adsorption (4,10,13,14). In an attempt to gain a better understanding of the role that the spinel phase ($MnFe_2O_4$) plays in Mn-Fe catalysts, a TPD study of Mn-Fe catalysts was conducted.

EXPERIMENTAL

$MnFe_2(C_2O_4)_3$ was prepared as described by Wickhem (15). The catalyst precursor $MnFe_2(C_2O_4)_3$ was calcined in air at different temperatures (1300, 1000, 700, and 500 ^oC) for 5 hours, followed by quenching in nitrogen. Fe_2O_3 was prepared from the precursor $Fe(C_2O_4)$ by calcining at 500 ^oC for 5 hours, followed by quenching

in nitrogen.

High purity argon, hydrogen, and carbon monoxide were used in this study. Gas flow rates of 30 ml/min were used for experiments conducted in this study. A temperature-programmed, catalyst characterization system (AMI-1) manufactured by Altamira Instruments, Inc., was used to obtain the TPD spectrum. A ramp of $15^{\circ}C$/min was used for all experiments in this study.

Catalyst samples were first exposed to a stream of argon gas at $120^{\circ}C$ for one hour, then they were reduced in hydrogen at $350^{\circ}C$ or $450^{\circ}C$ for 12 hours. The catalyst was cooled under flowing hydrogen from the reduction temperature to ambient temperature, flushed in argon for one-half hour to remove the weakly held hydrogen, then heated to $650^{\circ}C$ and held at $650^{\circ}C$ for one-half hour. The TPD spectra obtained from this sequence are referred to as high temperature (HT) H_2-TPD. After being purged with argon at $650^{\circ}C$ for about one-half hour, the catalyst samples were then cooled to ambient temperature. The catalysts were exposed to adsorbate gas (H_2 or CO) at ambient temperature for one hour, followed by flushing in argon for one-half hour, and then heated in argon to $650^{\circ}C$ and held for one-half hour. The TPD spectra obtained from this sequence are referred to as low temperature (LT) H_2 (or CO)-TPD.

RESULTS AND DISCUSSION

The amount of hydrogen absorbed (or desorbed) was determined from the TPD spectra shown in Figs 1 to 3. The effects of varying cal-cination and reduction temperatures on hydrogen uptakes are pre-sented in Table 1. For each catalyst, two hydrogen uptakes are measured. One is determined from the HT H_2-TPD, and the other is calculated from the LT H_2-TPD. Three to 50 times as much hydrogen uptake is obtained by comparing the HT H_2-TPD to that of LT H_2-TPD. Based on these two hydrogen uptakes at any reduction temperature, it is apparent that hydrogen adsorption is an activated process over Mn-Fe catalysts. These data are in agreement with previous studies that have shown hydrogen adsorption on iron catalysts can be highly activated (3,13). Noticeably, a high temperature of reduction significantly suppresses the amount of HT-H_2 uptake obtained from the MnFe1300 catalyst (Table 1). This result cor-relates well with our reaction data that there is a higher syngas conversion of 28% from the MnFe1300 catalyst with a lower reduction temperature, $350^{\circ}C$, versus that of 21% when the catalyst was reduced at $450^{\circ}C$ (16). The lower uptakes of hydrogen obtained from higher reduction temperatures may be a result of catalyst sintering and/or MnO encapsulated with iron particles during the higher temperature of reduction. The MnO encapsulated with iron particles has been verified by our XPS observations (16).

XRD results obtained for each of the catalysts are also shown in Table 1. These results show that various phases can be formed by calcination at different temperatures, as anticipated. High calcination temperature ($1300^{\circ}C$) favored the formation of a Mn-Fe

193

spinel before reduction. A mixture of spinel, manganese oxide, and iron oxide was observed when catalysts were calcined at 1000°C. Lower calcination temperatures (700 and 500°C) led to the formation of manganese oxide and iron oxides.   Different reduction temperatures can also result in the formation of different phases. In general, two phases, MnO and Fe, were observed when catalysts were reduced at 450 and 350°C. However, the additional spinel phase ($MnFe_2O_4$) formed when the catalysts were calcined at 1000 or 1300°C and reduced at 350°C. These results are consistent with previous studies on the effects of reduction temperature on spinel phases.   Studies on the Mn-Fe catalysts, prepared by the coprecipitation method, indicated that reducing catalysts at a higher temperature than 375°C results in the complete decomposition of the spinel phase to MnO and metallic Fe phases. however, reduction at a lower temperature than 375°C results in a mixture of Fe, MnO, and mixed spinel phases (3,5-7,9). Fe was the only phase observed after the reduction of the Fe500 catalyst prepared using the oxalate precursor.

Figs 1 and 2 illustrate the effects of calcination and reduction temperature on HT H_2-TPD of Mn-Fe catalysts.   Some general observations can be made by comparing the TPD spectra with the XRD results in Table 1.   Two desorption peaks (90 to 120°C and 450 to 510°C) can be correlated with the Fe phase (Figs 1a, 2a).   As indicated by XRD results, MnO and Fe phases were the only two phases present when catalysts were reduced at 450°C.   By correlating TPD spectra in Figs 2b to 2e with XRD results, the MnO-related peaks can be assigned as those peaks with temperatures near 140 to 190°C and 570 to 630°C. These MnO-related peaks were also observed in Figs 1c and 1d.   The XRD results also indicate that when catalysts are calcined at 1000 or 1300°C and reduced at 350°C, the spinel phase ($MnFe_2O_4$) is present along with MnO and Fe phases. The shapes of the TPD spectra for these materials (Figs 1c and 1d) are significantly different from other spectra in Figs 1 and 2, in that they have an additional peak centered at 350°C.   This additional peak, centered at 350°C, can be clearly correlated with the spinel phase ($MnFe_2O_4$). The surface of the Mn-Fe catalyst is probably complex.   However, through a systematic series of experiments, the Fe, MnO, and $MnFe_2O_4$ related TPD spectra can be assigned.   Fig. 3 shows the effects of calcination and reduction temperatures on LT H_2-TPD of Mn-Fe catalysts. Noticeably, the LT H_2-TPD spectra are much smaller than that in Figs 1 and 2. Combining the TPD spectra on Fig. 3 with the XRD information obtained in Table 1, the following conclusions were reached. The peak centered at 100°C is correlated with the Fe phase (Fig. 3). A broad desorption peak centered at 230°C may be correlated with the MnO phase (Figs 3a, 3b, and 3c).   The spinel phase related peak (with peak temperature centered at 350°C in Figs 1c and 1d) was also observed in Figs 3-c and 3-d. Based on the information collected from Figs 1 to 3, the spinel phase does adsorb hydrogen and it is an activated process. Weatherbee et al. indicated that highly activated adsorption of hydrogen on reduced iron could lead to hydrogen-adsorption limiting kinetics and a hydrogen-poor surface resulting in the modification of the product distribution

194

during hydrogenation (13). Less adsorbed hydrogen that may be available for the hydrogenation on the Mn-Fe catalysts under reaction conditions thus could favor the formation of olefins. Moreover, an additional experiment was conducted to verify the hypothesis that the spinel phase does adsorb hydrogen. The pure spinel, $MnFe_2O_4$, was first heated to 650°C in argon to desorb any impurities that remained during the preparation. Then the catalyst was cooled to 280°C in argon, followed by exposure to hydrogen for 10 minutes at 280°C. It was cooled down to ambient temperature in hydrogen, then switched to argon. The TPD spectrum obtained from this experiment showed only one desorption peak, centered at 350°C, which was identified as the spinel phase related hydrogen desorption peak previously identified.

The LT CO-TPD spectra are shown in Fig. 4. It was found that all the desorption peaks consisted solely of carbon monoxide. Based on the observed peaks, two forms of desorbed CO could be distinguished; one type desorbed at a temperature of about 90 to 110°C and the other at about 590 to 630°C. Both desorption peaks can be correlated with the Fe phase. The lower temperature peak is probably related with the desorption of molecular CO, whereas the higher temperature peak might correlate with the recombination of surface carbon and surface oxygen. The two desorption peaks are consistent with previous studies (4,12). It is interesting to note that the relative ratio of the higher temperature peak versus the lower temperature peak is affected by the reduction temperature (Fig. 4b to 4d and 4e to 4c). A larger ratio is obtained from Fig. 4b and 4e, when the catalyst is reduced at 350°C, while a smaller ratio is observed from Fig. 4d and 4c, when the catalyst is reduced at 450 oC. This difference in relative ratio correlates well with the reaction results (16). The CO conversion for the MnFe1300,350 catalyst (Fig. 4b) was 23%, while the conversion for the MnFe1300,450 catalyst (Fig. 4d) was 17%. These reaction results indicate that the lower reduction temperature catalyst has a higher CO conversion. The higher relative ratio of the two TPD peaks, obtained from the lower reduction temperature material (Fig. 4b) suggests that the CO dissociation is enhanced at lower reduction temperature. The peak around 230 to 250°C may be correlated with the MnO-related phase from Figs. 4c and 4d. No spinel phase related peak could be assigned in Fig. 4b and 4e. From the CO TPD spectra, it can be inferred that the spinel phase does not adsorb CO at room temperature. An additional experiment was also con-ducted to verify the hypothesis that the spinel phase does not adsorb CO. The pure spinel phase was first heated to 650°C in a stream of argon to remove any impurities. Then the catalyst was cooled to 280°C and the CO was introduced to the catalyst and held for 10 min followed by cooling to room temperature in CO. The flow was then switched to a stream of argon. The TPD spectrum obtained from this experiment showed no desorption of CO. An attempt was also made to verify whether or not the spinel phase alone is an active phase for syngas conversion. The $MnFe_2O_4$, which had been calcined at 1300°C for 5 hours from the spinel precursor, was exposed to synthesis gas at 280°C and 21 bar. In the absence of a reduction stage, it exhibited no activity during the 72-hour

195

testing period. The phase of the catalyst after calcination was shown to be a $MnFe_2O_4$ spinel (Table 1). After exposing the catalyst to synthesis gas, the phase was still a $MnFe_2O_4$ spinel, as determined by X-ray diffraction. These results suggest that the $MnFe_2O_4$ spinel phase is not responsible for syngas conversion when it is present alone. It is speculated that the lower electron density on the catalyst surface is responsible for this effect. It is well known that the $MnFe_2O_4$ spinel is a near normal spinel in structure. Fe^{+++} ions are distributed on both tetrahedral sites and octahedral sites in a 1:9 ratio. Fe^{+++} differs from Fe^O mainly in its lower electron density (11). Hence, electron back donation from the Fe^{+++} ions into the 2π orbitals of CO is too weak to involve a metal-carbon bonding. A metal-carbon bonding is a prerequisite for syngas conversion, and therefore, no reaction takes place.

CONCLUSION

In the light of the TPD spectra, XRD results, and our reaction results, we have concluded that $MnFe_2O_4$ may not be an active phase itself during FT synthesis, because it does not chemisorb CO. The $MnFe_2O_4$ phase does chemisorb hydrogen in an activated process. The temperature of reduction determines the phases of the Mn-Fe catalyst. The hydrogen adsorption over the Mn-Fe catalysts is an activated process and at least three types of adsorption state may be assigned, namely Fe, MnO, and $MnFe_2O_4$ related phases.

ACKNOWLEDGMENTS

REFERENCES

1. I.S.C. Hughes, J.O.H. Newman, Appl. Catal. 30,303,1987.
2. U. Lochner, M. Papp, M. Baerns, Appl. Catal. 23,339,1986.
3. J. Venter, M. Kaminsky, G.L. Geoffroy, and M.A. Vannice, J. Catal. 103,450,1987.
4. K.B. Jensen, and F.E. Massoth, J. Catal. 92,98,1985.
5. G.C. Maiti, R. Malessa, M. Baerns, Appl. Catal. 5,151,1983.
6. G.C. Maiti, R. Malessa, U. Lochner, H. Papp, M. Baerns, Appl. Catal. 16,215,1985.
7. J.Venter, M. Kaminsky, G.L. Geoffroy, M.A. Vannice, J. Catal. 105,155,1987.
8. K.M. Kreitman, M. Baerns, J.B. Butt., J. Catal. 105,319,1987.
9. R. Malessa, and M. Baerns, Ind. Eng. Chem. Res. 27,279,1988.
10. K.H. Huang, X.M. Zerg, J.T. Li, J. Catal. 81,259,1983.
11. H. Yoo and H. L. Tuller., J. Phys. Chem. Solid., 49,761,1988.
12. Y. Amenomiya, and G. Pleizier, J. Catal. 28,442,1973.
13. G.D. Weatherbee, J.L. Rankin, C.H. Bartholomew, Appl. Catal. 11,73,1984.
14. J.L. Rankin, C.H. Bartholomew, J. Catal. 100,533,1986.
15. D.G. Wickhem, "Inorganic Synthese"; Vol. 9,152,1967.
16. V.U.S. Rao, R.J. Gormley, S. Pollack, B. Zhong, in preparation

Table 1. Calcination and Reduction Temperature Effects on Catalyst Compositions and Hydrogen Uptakes.

Catalyst	Calcined Temp. °C	XRD[c]	Reduction Temp. °C	XRD[d]	HT-H$_2$[a] Uptake ml/g	LT-H$_2$[b] Uptake ml/g
Fe500	500	Fe$_2$O$_3$	350	Fe	2.58	0.12
MnFe500	500	Fe$_3$O$_4$, Mn$_2$O$_3$, Fe$_2$O$_3$	350	MnO, Fe	3.92	0.49
MnFe700	700	Mn$_2$O$_3$, Fe$_2$O$_3$	350	MnO, Fe	2.13	0.15
MnFe1000	1000	MnFe$_2$O$_4$, Mn$_2$O$_3$, Fe$_2$O$_3$	350	MnFe$_2$O$_4$, MnO, Fe	2.05	0.21
MnFe1300	1300	MnFe$_2$O$_4$	350	MnFe$_2$O$_4$, MnO, Fe	2.65	0.27
Fe500	500	Fe$_2$O$_3$	450	Fe	1.68	0.03
MnFe500	500	Fe$_3$O$_4$, Mn$_2$O$_3$, Fe$_2$O$_3$	450	MnO, Fe	3.03	0.95
MnFe700	700	Mn$_2$O$_3$, Fe$_2$O$_3$	450	MnO, Fe	2.23	0.3
MnFe1000	1000	MnFe$_2$O$_4$, Mn$_2$O$_3$, Fe$_2$O$_3$	450	MnO, Fe	2.48	0.11
MnFe1300	1300	MnFe$_2$O$_4$	450	MnO, Fe	1.77	0.29

[a] Obtained after the temperature-activated adsorption from the strem of hydrogen at reduction temperature and cooling to ambient temperature in the stream of hydrogen (HT H$_2$-TPD).
[b] Obtained after adsorption from the stream of hydrogen for one hour at ambient temperature (LT H$_2$-TPD).
[c] Obtained after calcination.
[d] Obtained after the reduced samples were mixed with Dow Corning silicone grease in a glove box for preventing further oxidation.
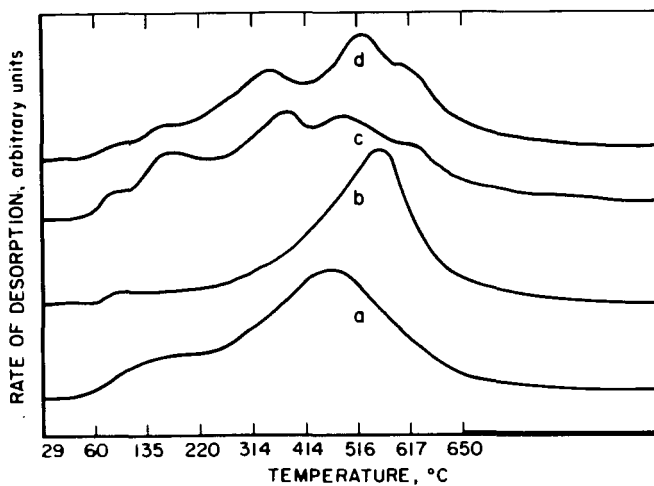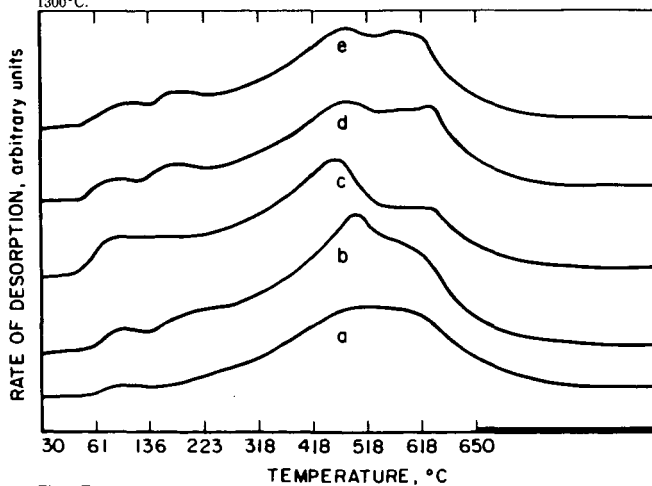
Fig. 1. Temperature-programmed desorption spectra of hydrogen (HT H$_2$-TPD) from catalysts as a function of calcination temperatures (catalysts were reduced at 350°C). (a) Fe$_2$O$_3$ calcined 500°C; (b) MnFe500 calcined 500°C; (c) MnFe1000 calcined 1000°C; (d) MnFe1300 calcined 1300°C.

Fig. 2. Temperature-programmed desorption spectra of hydrogen (HT H$_2$-TPD) from catalysts as a function of calcination temperatures (catalysts were reduced at 450°C). (a) Fe$_2$O$_3$ calcined 500°C; (b) MnFe500 calcined 500°C; (c) MnFe700 calcined 700°C; (d) MnFe1000 calcined 1000°C; (e) MnFe1300 calcined 1300°C.
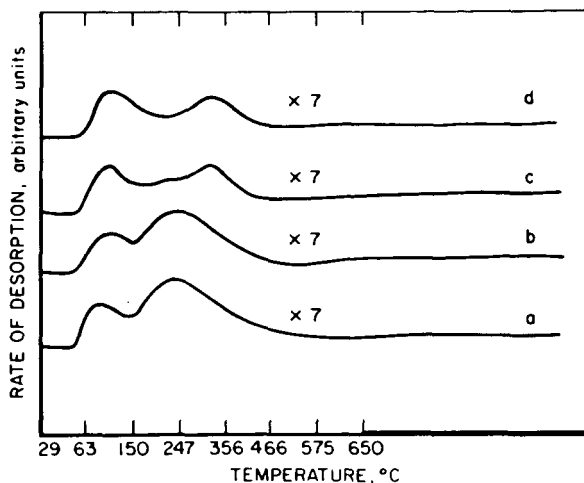
198

Fig. 3. Temperature-programmed desorption spectra of hydrogen (LT H_2-TPD) from catalysts as a function of calcination temperatures. (a) MnFe700 calcined 700°C, reduced 450°C; (b) MnFe1300 calcined 1300°C, reduced 450°C; (c) MnFe1000 calcined 1000°C, reduced 350°C; (d) MnFe1300 calcined 1300°C, reduced 350°C.
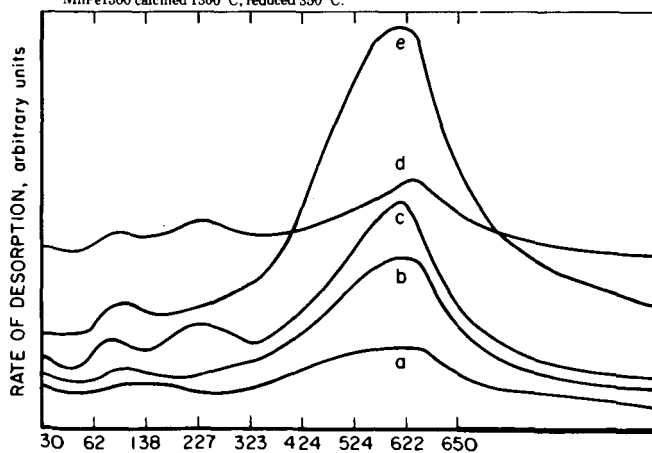

Fig. 4. Temperature-programmed desorption of spectra of carbon monoxide (LT CO-TPD) from catalysts as a function of calcination temperatures and reduction temperatures. (a) Fe_2O_3, 350 calcined 500°C reduced 350°C; (b) MnFe1300, 350 calcined 1300°C reduced 350°C; (c) MnFe1000, 450 calcined 1000°C reduced 450°C; (d) MnFe1300, 450 calcined 1300°C reduced 450°C; (e) MnFe1300, 350 calcined 1300°C reduced 350°C.